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CATALYTIC OXIDATION OF METHANE

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Forrest Everett Kendall

ENTITLED Catalytic Oxidation of Methane

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry.

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Forrest Everett Kendall.

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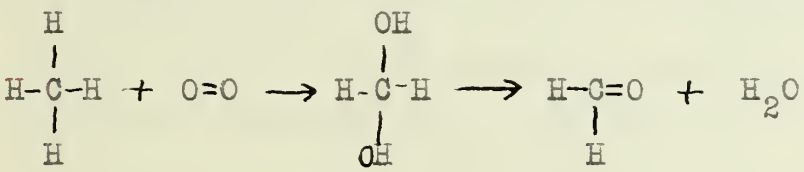
INTRODUCTION.

Statement of problem:

The partial oxidation of methane giving methyl alcohol and fomaldehyde as products is a problem the successful solution of which would lead to important commercial application. Large supplies of methane in the form of natural gas exist in this country, and successful solution of this problem would make this gas available as a cheap source of methyl alcohol and formaldehyde, both of which are finding ever increasing uses in industry. The greater part of the work dealing with the catalytic oxidation of methane to alcohol and formaldehyde is found in the patent literature. The object of the work presented in this paper was to investigate some of the processes discussed in the patents and more expecially to investigate the catalytic effect of metals and metallic oxides upon the oxidation of methane.

THEORETICAL and HISTORICAL.

The question as to how the methane is attacked by oxygen during oxidation is one of the greatest importance in this problem. Does the oxidation proceed by sucessive hydroxylization of the methane molecule followed by dehydration or is the whole molecule oxidized simultaneously? The mechanism of this reaction was studied rather extensively by Bone and Whaler.[1] Passing a mixture of methane and oxygen rapidly through a bor-silicate glass tube at a temperature of 500°C for a period of ten days and removing the intermediate products of combustion by a system of scrubbers, they were able to obtain yields of 20% of formaldehyde but no trace of methy alcohol. They conclude that the oxidation of methane proceeds in the following manner.



$$HCHO + O_2 \rightarrow H_2O + CO_2$$

$$2HCHO + O_2 \rightarrow H_2O + 2CO$$

They believe the intermediate formation of CH_3OH is extremely doubtful at this temperature. However the evidence presented by them cannot be considered conclusive when one considers the catalytic effect of glass upon the dehydrogenation of alcohols at temperatures even below those used in this experiment.

1. J.C.S. T(1902) 535 - T(1903) 1075

$CH_3OH \longrightarrow HCHO + H_2$

The only conclusion that can be drawn is that if methyl alcohol is formed its decomposition into formaldehyde at this temperature is extremely rapid.

Proof that methyl alcohol is an intermediate product in the oxidation of methane is given by oxidizing the methane at lower temperatures with more active oxidizing ag agents. Otto[2] showed that when methane was oxidized by ozone at room temperature, methyl alcohol, formaldehyde and formic acid were the principal products. However if the oxidation was carried out above 100°C only formaldehye and formic acid was formed. Evidently the reaction

$$CH_3OH \xrightarrow{\Delta} HCHO + H_2O$$

is greatly accelerated by a slight increase in temperature. Lance and Elsworthy[2] claim the production of methyl alcohol, formaldehyde and formic acid from methane using hydrogen peroxide or persulfuric acid as an oxidant in the presence of ferrous sulfate as a catalyst.

In both of the above cases the active oxidizing agent is probably atomic oxygen, the ferrous salt serving to accelerate the decomposition of the peroxides in the second case.

$$O_3 \rightarrow O_2 + O$$

$$H_2O_2 \rightarrow H_2O + O$$

2. Ann. Chim. phys. 1898VII.13 77-144. 2. B.P.7297 1916

$$H_2S_2O_8 + H_2O \rightarrow 2H_2SO_4 + O$$

In order then to obtain methyl alcohol from methane the process would have to be carried out at a low temperature. Formaldehyde may be obtained at much higher temperatures but the yield decreases with an increase in temperature. Thus the yield obtained by Bone and Wheeler at 500° C. was 20% while Glock[3] by rapidely cooling the products of combustion at 800°C was able to obtain only traces of formaldehyde.

It would seem from consideration of volume and heat changes that the Le'Chatelier principle could be applied to this reaction.

$CH_4 + 1/2\ O_2 \rightarrow CH_3OH + 42,900$ Cal. 1/2 mole decrease

$CH_3OH + 1/2\ O_2 \rightarrow HCHO + H_2O + 33,000$ Cal. 1/2 mole increase

$HCHO + 1/2\ O_2 \rightarrow CO + H_2O + 20,000$ Cal. 1/2 mole increase

$HCHO + O_2 \rightarrow CO_2 + H_2O + 137,000$ Cal. no change.

It would seem that an increase in pressure would shift the equilibrium point of the first reaction to the right, the equilibrium points of the second and third reactions to the left, while it would have no effect upon the last one. An increase in temperature would favor the third reaction, while it would shift the equilibrium point of the others to the left.

However very little importance can be given to these considerations as the equilibrium point is never reached.

Indeed it is not desirable to reach the equilibrium point for there all conditions would favor the decomposition of any methyl alcohol and formaldehyde. If the space velocity of the gases over the catalyst is not high the dehydrogenation of these products tends to occur. The problem is one that involves the acceleration of the first two reactions and depressing the velocity of the last two rather than one that involves equilibrium points.

In choosing a catalyst for this reaction there are several points to be considered. First: the catalyst must be able to furnish oxygen to the reaction in a more active state than atmospheric oxygen so that the reaction may proceed at as low a temperature as possible. Second: the catalyst must not accelerate secondary reactions such as the dehydration and dehydrogenation of the methyl alcohol and formaldehyde.

The first condition might be met by metals that have the property of forming more than one oxide, thus permitting the assumption of an oscillating oxide as an oxygen carrier.

$Fe_2O_3 \longrightarrow Fe_2O_2 + O$

$2CuO \longrightarrow Cu\ O + O \rightarrow 2Cu + O$

Thus a large list of metals having more than one oxide might be tried as fulfilling this condition as platinum, iron, nickel, cobalt, tin, copper, manganese, vanadium, chromium, uranium, etc. if it were not for secondary reactions.

3. DRP 107014.

All of these metals are effective catalysts for the following reactions:

$CH_3OH \rightarrow HCHO + H_2$

$HCHO \rightarrow CO + H_2$

especially at elevated temperatures.

Even in the case of copper which is less active in this respect than most of the others the decomposition into carbon monoxide and hydrogen is practically complete at 350° at low space velocities. However if proper space velocities are used with copper as a catalyst methyl alcohol can be oxidized to formaldehyde giving a yield of over 70%,[4] showing that so far as the secondary reactions are concerned copper could be used as a catalyst in the oxidation of methane to formaldehyde. One would not expect to obtain any methyl alcohol with such a catalyst. This secondary reaction would prevent the use of iron, cobalt, nickel and the platinum metals as catalysts in this reaction.[5]

The above conclusions are embodied in a number of p patents.

Glock[6] in 1898 suggested the passage of methane and air over granulated copper at 800° C.

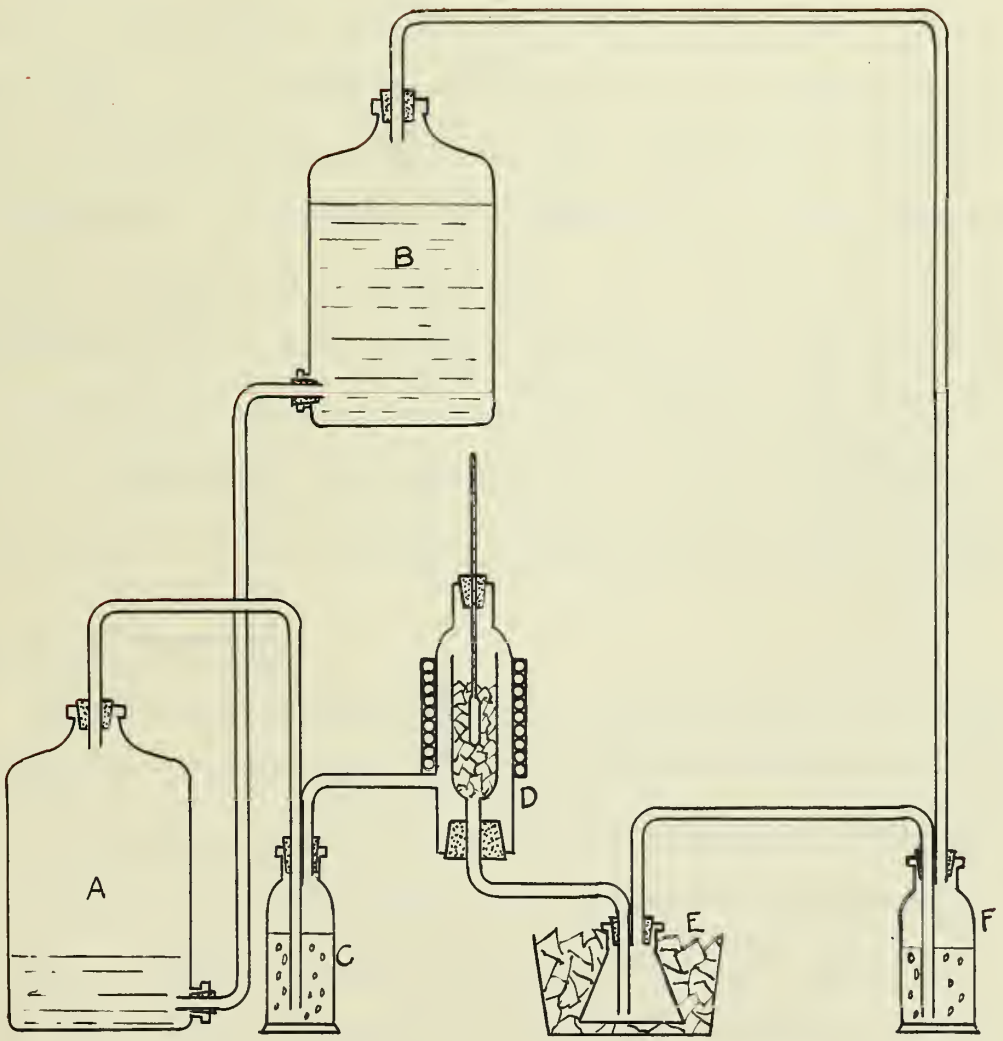
Blackmore[7] in 1904 states than methane passed over certain oxides yields methyl alcohol at 128°C and formaldehyde at 160°C. The yields in both cases were placed at 90%. The oxides used were CuO, Fe_3O_4, MnO_2 and BaO_2.

4. Hochstater B.P. 464/1914. 5. Rider and Taylor p. 128
6. D.R.P. 107,014 7. U.S.P. 774,824. 8. D.R.P. 214,155
D.R.P. 286,731 1906

Another German patent states that formaldehyde is formed if methane and a large excess of moist air is passed over metallic copper of silver or both. The formaldehyde may be removed and the mixture passed over the catalyst repeatedly.[i]

One of the more novel catalytic agents proposed was tan bark. The Sauerstoff and Stickstoff Ind.[8] and V.Unruh[9] claim that the oxidation of methane by air takes place at 30 - 50° C. in the presence of such material. It is probable that the aldehyde itself was derived from the tanbark.[10]

i. D.R.P. 286,731 Augeo '13
8. D.R.P. 214,155/1906
9. U.S.P. 891,753/1907
10. Rideal and Taylor 131.


A
B
C
D
E
F

EXPERIMENTAL.

The Preparation of Methane.

The methane used in this work was prepared by the soda-lime fusion of sodium acetate.

$$CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$$

Freshly fused sodium acetate was heated with soda-lime in a pyrex flask. The methane obtained by this process was impure being contaminated by acetone, some unsaturated hydrocarbons, and hydrogen. The acetone and unsaturated hydrocarbons were removed by passing the gas slowly first through acid potassium permanganate and then through concentrated sulfuric acid. The purified methane contained some hydrogen but this would have no effect upon the experiment as it was oxidized in most cases upon the first passage of the gas over the catalyst.

Method of Procedure.

The methane stored in bottle A was passed in certain experiments through wash bottle C filled with sulfuric acid to dry the gas, in other experiments through a wash bottle filled with water maintained at a constant temperature so as to insure certain constant concentrations of H_2O in the gas. It was then passed through the catalyst contained in an apparatus electrically heated. The apparatus used was one described by Rideal and Taylor.[11] After passing through the catalyst it was passed through a flack immerged in an ice bath to condense the water together with any methyl alcohol which may have been formed. The gas was then passed through

11. R. and T. p. 72.

a wash bottle filled with water to remove any formaldehyde. The gas was then lead back to gas bottle B.

The gas was forced through the apparatus at varying speeds, the most usual speed being about 20 liters per hour. When the gas in A was completely forced out into B the positions of the bottles was reversed.

At the end of the run the contents of E and F were examined for formaldehyde and methyl alcohol.

Preparation of the Catalyst.

Copper nitrate was precipitated by NaOH and the copper hydroxide changed into CuO by boiling; after filtering the oxide was dried at 200° and then washed and redried. In some experiments CuO was precipitated upon asbestos fibre as a support.

In the experiments using metallic copper some of this CuO was reduces in the catalysis vessel with hydrogen.

In certain experiments Copper-silver couples were used. They were prepared by igniting CuO moistened with $AgNO_3$ solution and reducing with hydrogen.

Nickel oxide was prepared by igniting a mixture of nickel nitrate and sugar. The oxide was obtained in a very porous form. In some of the experiments this nickel was reduced with hydrogen.

Iron oxide was prepared by igniting iron filings.

Results.

I. Mixtures of equal volumes of dry methane and oxygen.

Metallic Copper as a catalyst.

Temperature	Effect upon Catalyst	MeOH	HCHO
50° C.	No effect	None	None
100°	" "	"	"
150°	" "	"	"
200°	" "	"	"
250°	Slowly oxidized	"	"
300°	Oxidized	"	"
350°	"	"	"
400°	Oxide reduced	"	Trace.

Passed over metallic Cu heated to reddness no trace of HCHO.

II. One volume of Methane , 2 volumes of Oxygen.

Cu as catalyst.

50°-200°	No effect	None	None
300°	Cu oxidized	"	"
350°	" "	"	"
400°	" "	"	"
Red heat	" "	"	"

III. One volume of Methane-1 volume of air.

50° - 200°	No effect	"	"
300°	" "	"	"
350°	Cu oxidized	"	"
400°	Oxide reduced	"	Trace
Red Heat	" "	"	"

IV. Equal volumes of Methane and Oxygen.

Cu, Ag couple as catalyst.

Same results as with Cu alone.

V. Ni_2O_3 and Fe_2O_3 as catalysts.

No reduction of catalyst apparent and no formaldehyde formed up 400° C.

VI. Methane alone. CuO as Catalyst.

Temp.	Effect on Catalyst.	MeOH	HCHO
50°-300° C.	No effect	None	None
350°	Slow reduction	''	''
400°	Reduction to metal	''	''

VII. Methane Air Steam.

Cu as Catalyst.

50° - 200°	No effect	None	None
300°	Cu oxidized	''	''
350°	'' ''	''	''
400°	Oxide reduced	''	Trace.

CONCLUSION.

So far as can be judged by the experimental results it is impossible to obtain any methyl alcohol from the oxidation of methane using metals or metallic oxides as catalysts. The claims of Blackmore of yields of 90% methyl alcohol from the oxidation of methane appear to be unfounded. His claims of 90% yields of formaldehyde also seem to be much larger than the results of this work would indicate.

It would seem that the metals and metallic oxides studied exert about the same catalytic action upon the combustion of the formaldehyde as upon the combustion of methane to formaldehyde for no greater traces of formaldehyde could be found than in the suddenly cooled gases from a methane flame.

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